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THE EFFECTS OF SOL-GEL SILICATES ON HYDRATION KINETICS AND MICROSTRUCTURE OF PORTLAND CEMENT SYSTEMS

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ABSTRACT: The effects of sol-gel silicates on Portland cement hydration were investigated. Silica sols were realized by tetraethylorthosilicate, triethoxymethylsilane, ethanol, water and nitric acid or ammonia. Solvent-free sols were also synthesised. The prepared sols were mixed with cement pastes at a w/c of 0.4 or 0.5 at varying doses of 0.5–10% by mass of dry cement. The solvent-free synthesised sol appeared to be a more suitable candidate. This is because observation of the hydration kinetics revealed a shortening of the dormant phase of cement hydration and exhibited a higher power output during this stage, representative of additional nucleation sites created in the system. However, the main peak power output that occurs at the end of acceleratory stage was decreased, further pronounced at higher sol dosages. This can be attributed to the ethoxy-based precursor, which produces ethanol as a by-product of hydrolysis reactions. It is therefore of great interest to investigate possible routes to optimise the sols to limit the alcohol content. SEM analyses on fractured surfaces of 28 day old pastes revealed a distinctive morphology, particularly at higher sol dosages. The development of C-S-H on portlandite was observed, which further suggests that the sol-gel silicates could be providing additional nucleation sites [therefore](#), acting as a seeding agent.

Keywords: Silica, Sol-gel, Nanotechnology, Nucleation seeding, C-S-H polymerisation.

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INTRODUCTION

In light of the overriding imperative to reduce the carbon footprint, research in the recent decades has been underscored to improve the sustainability of cementitious materials. Primarily, this has been focused on limiting the amount of Portland cement (clinker content) in cement-based mixtures through various possible routes. These have included the use of chemical admixtures, inert fillers, supplementary cementitious materials, and optimization of aggregate size and content [1-4]. Enhancing the durability of cementitious materials, which are susceptible to degradation due to moisture ingress, aggressive ions, chemicals, abrasion or weathering, has persisted as another major challenge for material scientists.

Calcium Silicate Hydrate (C-S-H), a micro and nano-porous gel, is the most critical product of cement hydration and the major phase responsible for cohesion. Occupying over 60% by volume of the hydrated cement paste [5-7], it is a major contributor to the mechanical and physical properties, which include strength, shrinkage and permeability. Recent advances in nano-characterization techniques have led to an increased understanding of the nanostructure of C-S-H [6]. This has led to a promising new stream of research focused on the application of nanotechnology to modify and manipulate matter at a near atomic scale in efforts to develop superior and novel C-S-H systems [3, 7-9]. Several researchers have demonstrated that conventional cementitious materials exhibit radically improved properties when engineered at the nanoscale [10].

The term ‘seeding’ agents, or nucleation seeding, often refers to the use of pre-hydrated silicates for the modification of the hydration processes [11]. It has proved to be a useful approach to control the kinetics of cement hydration, most notably for acceleratory effects [JHI][12]. More importantly, it has also been recognised as a unique tool to tailor the overall composition of C-S-H and the micro and nanostructure of hydrated Portland cement. In particular, the seeding effect in silica-cement systems is rather well documented, and known to improve the strength, stiffness and the durability characteristics of cement-based materials. In addition to the pozzolanic properties, it is believed that particles of micro and nanosilica serve as nucleation sites for enhanced precipitation of C-S-H [12-19]. Accordingly, a more intricate and denser microstructure of C-S-H networks has been observed for silica supplemented cement systems [18, 20-23].

The important role of silica in the C-S-H framework is irrefutable. Careful examination of silica chemistry shows that the chemical reactions that occur during formation of the basic silicate species follow an almost identical pathway in the case of Portland cement hydration, pozzolanic materials and blended mixtures. It must also be emphasised that cement hydration displays many similarities to the synthesis processes of sol-gel silicates, and may be regarded as a special branch of inorganic polymerisation. Typically, sol-gel synthesis involves the hydrolysis and polycondensation of silicon alkoxide precursors using water, alcohol as a mutual solvent and a catalyst. Careful control of the processing parameters may provide the ability to produce cementitious systems that are low in carbon, more energy efficient and with greater resilience than conventional Portland cement based systems. This can be achieved by tailoring the degree of polymerisation of C-S-H to a higher level, which is expected to facilitate the ‘refinement’ of the micro and nanostructure. In addition, the increase in the silicate chain length within the C-S-H framework would also lead to a more stable matrix. In line with the objectives discussed above, the application of sol-gel technology to cementitious materials opens up the door to endless possibilities, both for research and industry.

In the current work, investigations were carried out to assess the prospect of employing sol-gel material as a seeding agent for Portland cement systems. In this regard, the effects of sol-gel silicates on cement hydration were examined. The parameters of the sol-gel synthesis were explored in order to elucidate the suitable candidates, and to gain an improved understanding with regards to the limitations. The synthesis parameters of importance include the molar ratio of the materials, type of silicon alkoxide precursors, nature and concentration of the catalyst, pH, temperature, amount of water, and synthesis duration. These parameters not only affect the [ageing process](#) (-sol-to-gel kinetics) and the resultant gel structure but also influence the overall behaviour of the sol-gel material as it interacts with Portland cement. In more detail, the kinetics of cement hydration and the effects on the microstructure of cement pastes [dosed](#)^[JH2] with sol-gel material were characterised by means of isothermal calorimetry and scanning electron microscopy.

EXPERIMENTAL

Synthesis of Sol-gel Silicates

For the synthesis of sol-gel silicates, tetraethoxysilane (TEOS) reagent grade 98% and triethoxymethylsilane (MTES) technical grade 90% supplied by Sigma-Aldrich were the two silicon precursors used. Nitric acid (HNO₃) puriss .p.a > 65% and ammonium hydroxide (NH₄OH) 28–30% NH₃ basis were used as the acid and base catalysts, respectively, also supplied by Sigma-Aldrich. Ethanol (EtOH) puriss. p.a ACS reagent 99.8% was employed as the mutual solvent, supplied by Fluka. Distilled water was used for all [sol](#)^[JH3] preparations. The molar ratios of the starting materials, synthesis parameters and duration are presented in Table 1. The formulations and parameters for sol-gel synthesis were adopted on the merits of low and high pH to investigate the two ranges of pH spectrum of the starting sols on cement hydration. The solutions were continuously agitated for the entire duration of the synthesis procedure. The prefix, A, as in the case of sol A1 denotes an acidic medium, and similarly a basic medium for sol B1. In order to mitigate the effects of alcohol on cement hydration, sols A2 and B2 were allowed to age in partially opened containers for one week prior to being used as admixtures. Sol N1 was synthesized without the use of a catalyst and without ethanol.

Table 1 Formulations and parameters for sol synthesis.

DESIGNATION ^[JH4]	TEOS	MTES	EtOH	H ₂ O	HNO ₃	NH ₄ OH	pH	TEMP	DURATION
A1	1	0.333	4	8	0.005	-	3.00	40°C	1.25 hr
B1	1	-	4	10	-	0.03	9.80	40°C	1.67 hr
A2	1	-	4	4	0.05	-	0.95	25°C	25 hr
B2	1	-	4	4	-	0.05	9.80	25°C	25 hr
N1	1	-	-	4	-	-	4.50	25°C	1 hr

Sol-gel Enhanced Cement Mixtures

The cement used in the present work was CEMI (BS EN 197-1:2011) with 95% OPC content and 5% minor additional constituents. Table 2 illustrates the mix design of the prepared specimens. Cement pastes were prepared at a predetermined water-to-cement ratio (w/c) of 0.4 or 0.5. The designation is assigned according to the sol that was used and the w/c ratio. For example, A1C1, the prefix indicates that sol ‘A1’ was used to prepare the cement pastes whereas the suffix ‘C1’ indicates that the w/c ratio was 0.4. Similarly, for A2C2, sol ‘A2’ was used and ‘C2’ represents a w/c of 0.5. Accordingly, the controls are designated simply as C1 or C2. A Standard mortar mixer conforming to BS EN 196-1:2005 was used at blade rotational speed of 285 min⁻¹ and planetary movement of 125 min⁻¹. Cement quantity was fixed for all cement pastes and the dosage of sol-gel material was varied at doses of 0.5, 1, 3 and 5% by mass of dry cement for sols A1 and B1. Given that the sols A2, B2 and N1 were optimised for lower alcohol content, dosages were increased to 1, 3, 5 and 10% by mass of dry cement. The higher percentage was used to augment the possible effects and to elucidate minor changes in the chemical and the microstructural properties. In some cases, particularly at high dosages, inhomogeneous mixing of the sol-gel material with the cement pastes was observed. In all cases, part of the prepared paste was immediately placed in a sample holder and analysed using isothermal calorimetry. The remainder was cast into 8x40x160 mm moulds for a 24 hour period and subsequently cured for 28 days under water at 20°C until microstructural characterisation.

Table 2 Mix design[JH5].

DESIGNATION[JH6]	SOL	CEMENT	W/C	DOSAGE (% BY MASS OF DRY CEMENT)
C1	-	CEMI	0.4	-
A1C1	A1	CEMI	0.4	0.5, 1, 3 and 5
B1C1	B1	CEMI	0.4	0.5, 1, 3 and 5
C2	-	CEMI	0.5	-
A2C2	A2	CEMI	0.5	1, 3, 5 and 10
B2C2	B2	CEMI	0.5	1, 3, 5 and 10
N1C2	N1	CEMI	0.5	1, 3, 5 and 10

Instrumentation

The kinetics of cement hydration was followed using a Calmetrix I-Cal 4000 calorimeter. The equipment was set to log data for a 52 hour period, sufficient to give enough [JH7]information on early hydration. Tests were carried out at a temperature of 20°C for all series of investigations.

Morphological changes were investigated using secondary imaging generated by a Joel JSM 6301F field emission scanning electron microscope. The protocol employed to prepare the samples for microstructural characterisation has been described elsewhere [18]. The as-prepared 28-day samples were fractured using a blade and the fracture surface coated with 20nm of chromium. The conductive coating permitted operating at higher accelerating voltages without the effects of ‘charging’, giving cleaner images at higher magnifications.

RESULTS

Kinetics of Cement Hydration (Isothermal Calorimetry)

The hydration kinetics of cement pastes A1C1 and B1C1 are presented in Figure 1 and Figure 2, respectively. In the case of A1C1 (Figure 1), cement pastes with the acid catalysed sol, the ‘dormant’ phase was extended and the peak power output decreased considerably, as the dosage was increased from 0.5% to 5%. Accordingly, a reduction in the total amount of energy released with increasing dosage during the period of 52 hours was observed. Cement pastes with 3% and 5% dose were significantly retarded.

For B1C1 (Figure 2), cement pastes with the base catalysed sol, as the dosage was increased from 0.5% to 5%, no lengthening of the dormant phase was observed but the main peak power output decreased. The deceleration stage was marginally lengthened. In more detail, an increase in dosage from 0.5 to 1% should have resulted in a further decrease in peak power output. Instead, an increase was noted. Likewise, the power plots for 0.5% and 3% dosages are very similar to each other. Accordingly, the total energy released over the 52 hour period is almost the same for the control and the sample with 1% dose, similarly for 0.5% and 3% dosages. A significantly increased level of activity during the dormant phase was noted when sol dosage was increased to 5%. Two distinct preliminary conclusions could be drawn. (i) Alcohol content in the sol is of primary concern and ‘inhibits’ cement hydration, that is, reduces the peak power output. (ii) The pH alone is not a limiting factor, the acid may be considered to be of secondary importance, which so far appears to ‘delay’ hydration, that is, shifts the peak power.

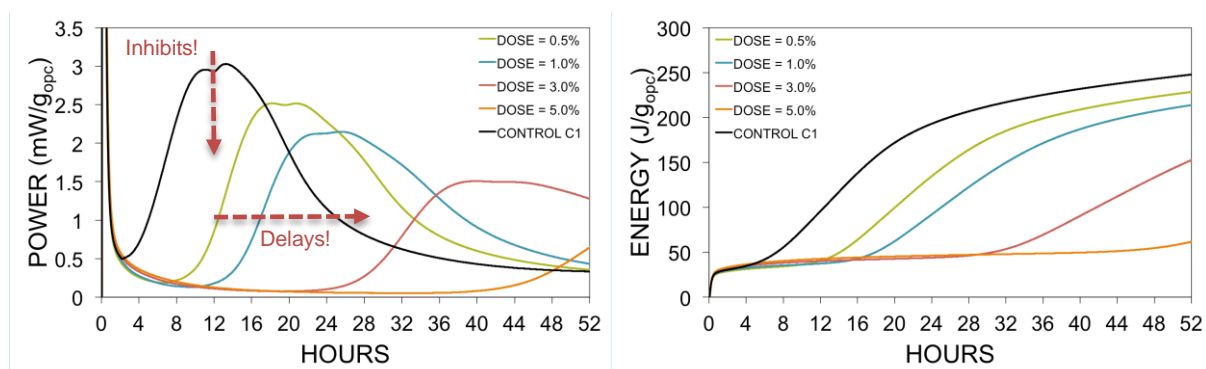


Figure 1 Hydration of cement pastes A1C1, (Left): Power output (Right): Cumulative energy.

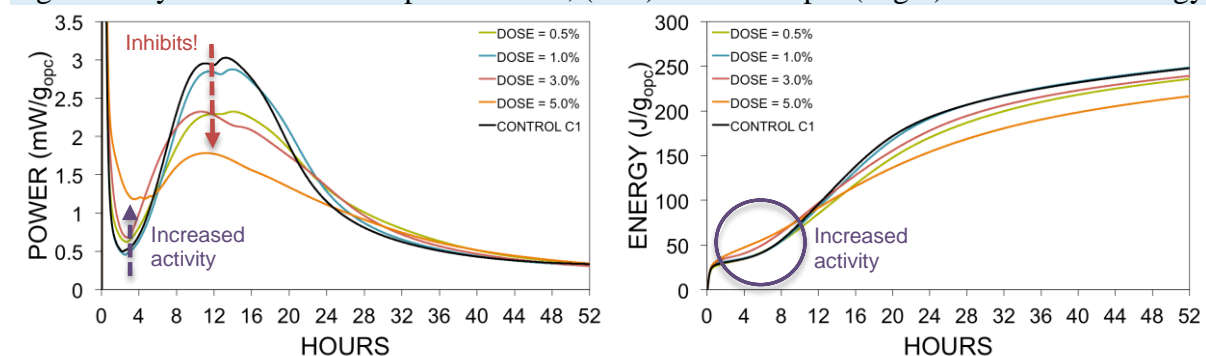


Figure 2 Hydration of cement pastes B1C1, (Left): Power output (Right): Cumulative

The hydration kinetics of cement pastes with the optimised sols, A2C2, B2C2 and the solvent-free synthesised sol N1C2 are presented in Figure 3, Figure 4 and Figure 5, respectively. In the case of A2C2 (Figure 3), cement pastes with the optimised acid catalysed sol, with increase in dosage from 1% to 10% a reduction in the peak power output was noted in comparison to control C2. Despite the higher sol dosages, the effects were less dramatic compared to A1C1 (Figure 1). Likewise, a lengthening of the dormant phase was observed, which was also less pronounced than A1C1. A significant lengthening of the deceleration stage occurred, particularly at higher sol-gel dosages. Overall, the cumulative energy plots of A2C2 illustrate that the post-synthesis ‘optimisation protocol’ of the sol A2 (1 week ageing in partially open containers) led to an improvement of cement hydration, when compared to A1C1. This is evident considering the higher energy evolved at the 52-hour mark. Speculatively, if the test continued to run for a longer duration of 72 hours, for 1% dosage, the total energy may have increased beyond that of the control. Further experimentation to validate this hypothesis is required. It is also worth mentioning that a direct comparison between A2C2 and A1C1 is limited to some extent, owing to the rather different formulations employed.

Considering B2C2 (Figure 4), cement pastes with the optimised base catalysed sol, with an increase in dosage from 1% to 10% a reduction in the peak power output was detected in comparison to control C2. These effects were more dramatic in comparison to B1C1 (Figure 2). Interestingly, despite the high pH of the sol, lengthening of the dormant stage occurred, which was more prominent at higher dosages. The paste with 10% dose was considerably retarded. This ‘delaying’ effect was not observed in the case of B1C1 (Figure 2). A direct comparison between B2C2 and B1C1 is limited to an extent due to the different formulations. It is however worth mentioning that in the case of B2C2, the sol was more concentrated with alcohol, due to the lower R-value ($\text{H}_2\text{O}/\text{Si}$) employed; despite the post-synthesis ‘optimisation protocol’ of the sol B2 (1 week ageing in partially open containers), it had a higher alcohol percentage in the dose applied. Collectively, the aforementioned observations support the initial hypothesis that alcohol ‘inhibits’ cement hydration and that pH alone is not a limiting factor. The power output plots of A2C2 (acidic sol) in Figure 3 and B2C2 (basic sol) in Figure 4, which can be directly compared owing to similar formulations employed, further support this view.

In the case of N1C2 (Figure 5), cement pastes with the solvent-free non-catalysed sol, as the dosage was increased from 1% to 10% a decrease in peak power output was noted. There were some discrepancies, for example when the sol dosage was increased from 3% to 5%, possibly due to inhomogeneous intermixing with the cement paste. A significant lengthening of the deceleration stage was detected, and more interestingly the extended ‘shoulder’ observed at the 28–36 hour mark in the case of 5% dose. As a result, the total energy evolved, appeared to increase at later stages, and may have superseded the value exhibited by the 1% dosed paste at the 72 hour mark had the data been recorded for the duration. Further experimentation to validate this is required. The 1, 3, and 5% dosed pastes exhibited a shortening of the dormant stage with an elevated power output in comparison to control C2, indicating possible additional nucleation of C-S-H. The hydration reactions were able to recover from the dormant phase, yet still not completely. The 10% dose led to a completely retarded cement paste, which can be rationalised by the following: (i) due to the short processing time and lack of a catalyst the unhydrolysed sol-gel precursors molecules were hydrolysed in the high pH environment of cement pastes, and the by-product of the sol-gel hydrolysis (alcohol) retarded the paste releasing alcohol and thereby retarding the paste, (ii) the unhydrolysed sol-gel precursor molecules were strongly adsorbed onto the clinker or the nucleated particles, preventing further dissolution of the clinker and precipitation of C-S-H. The cumulative energy

plot further supports this view [JH16] where the 10% dose revealed the highest total energy in the early stages (see Figure 5). Two possible methods to further optimise the sol N1 include (i) slightly longer synthesis duration for increased hydrolysis or employing a dilute catalyst solution, (ii) removal of the alcohol that is produced as a by-product of precursor hydrolysis.

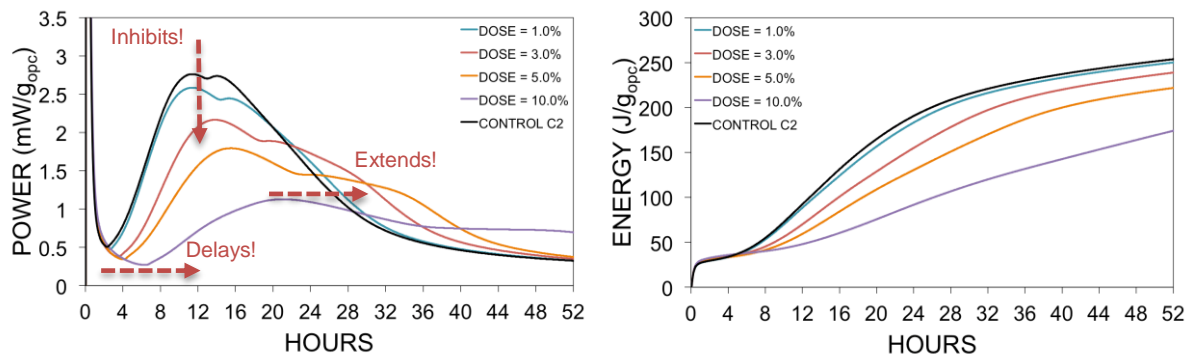


Figure 3 Hydration of cement pastes A2C2, (Left): Power output (Right): Cumulative energy.

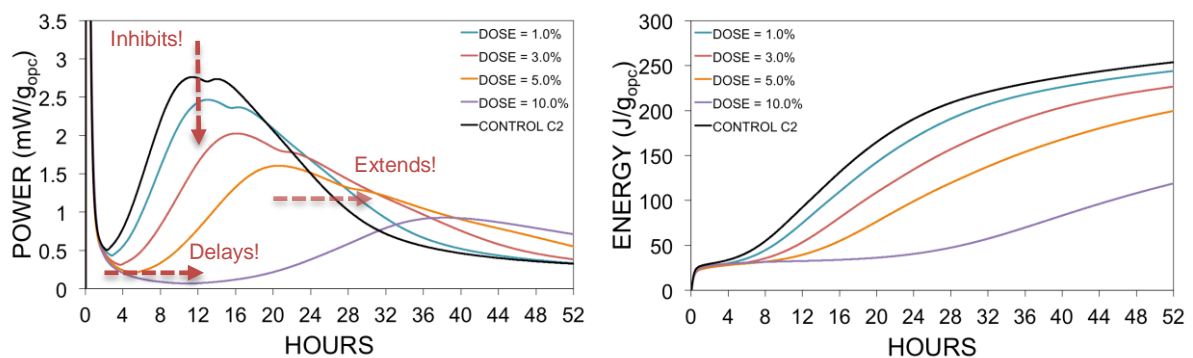


Figure 4 Hydration of cement pastes B2C2, (Left): Power output (Right): Cumulative energy.

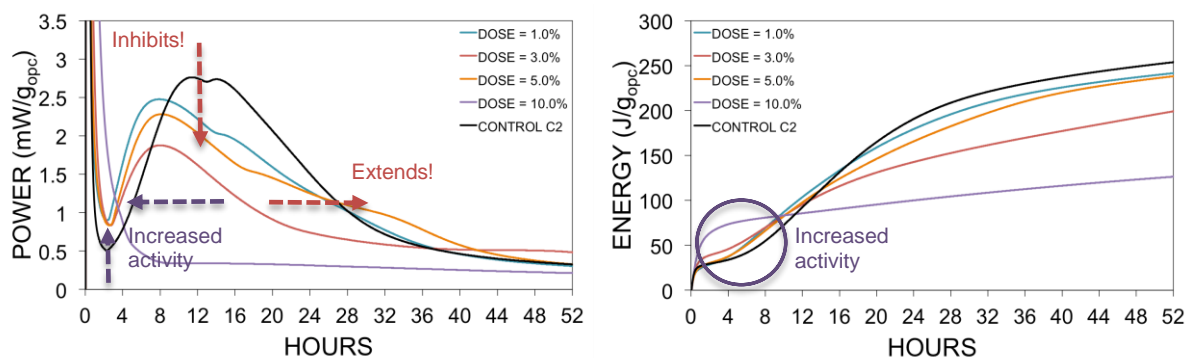


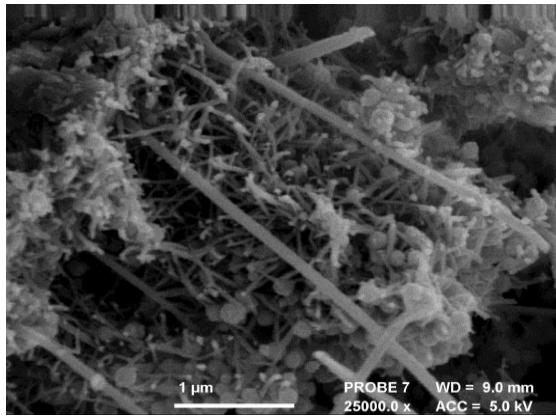
Figure 5 Hydration of cement pastes N1C2, (Left): Power output (Right): Cumulative energy.

Microstructure (scanning electron microscopy)

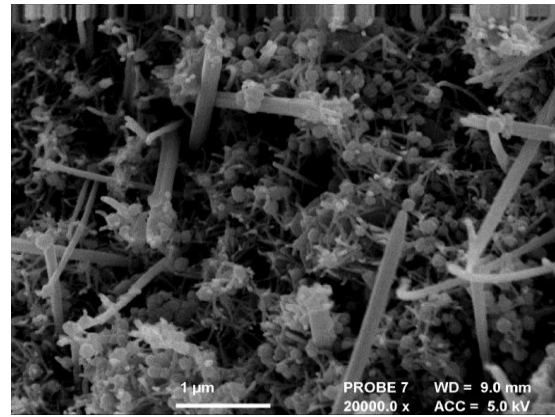
The microstructure of the sol-gel cement composites was investigated at 28 days to elucidate the differences in morphology of mature cement pastes. Investigations were carried out on all samples at 28 days. However, in light of the observed hydration kinetics that exhibited a shortening of the dormant stage along with an increased level of activity during this stage (see Figure 5), emphasis here is placed on cement pastes with the solvent-free non-catalysed sol (N1C2). At low magnifications no real distinctions could be made. Figure 6 displays SEM micrographs at high magnifications for the control C2 and N1C2 at doses of 1, 5 and 10%. With an increase in dosage, particularly at 5% and 10%, differences in morphology could be observed along with C-S-H nucleation.

For the control C2 at high magnification (Figure 6a), the long thin needles represent ettringite, whereas C-S-H can be seen as the fine smaller fibre-like structures. The tiny spherical particles were unexpected in the control sample, which can most likely be attributed to the minor additional constituents. The strong resemblance to micro and nanosilica particles is also worth pointing out. The microstructure and morphology for N1C2 dose 1% (Figure 6b) was almost identical to that of control C2, despite the calorimetry data indicating that some form of additional nucleation of C-S-H had occurred. In the case of N1C2 dose 5%, Figure 6c displays what appears to be dense C-S-H gel towards the right hand side of the protruding needles of ettringite. Closer examination at higher magnifications of the specimen, illustrated in Figure 6d, shows what appears to be C-S-H covered with dense clusters or particles, different than what was observed in Figure 6a and Figure 6b. Given the high percentage of the sol dosage, it could either be silica nanoparticles that precipitated at the high pH, or possibly a granular form of C-S-H observed at very low Ca/Si ratios, as also reported by He et al. [24]. The latter gains further prospect, given the power plot of the calorimetry data (Figure 5) that showed a shortening of the dormant phase with an increased level of heat output, representative of additional nucleation of C-S-H. Additionally, for N1C2 dose 5%, the C-S-H gel as observed in Figure 6c, or the granular agglomerations of C-S-H as shown Figure 6d, both, appear to form much denser pastes when compared to the control C2 and N1C2 dose 1%. This could lead to enhanced durability characteristics and performance.

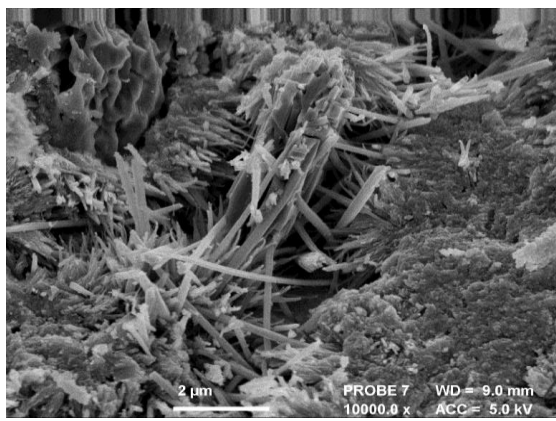
The micrograph for N1C2 dose 10%, shown in Figure 6e, displays a very distinct morphology, a reticular form of C-S-H being developed on a portlandite sheet, also intrinsic to low Ca/Si ratio (higher degree of C-S-H polymerisation). These appear to form rather intricate or interconnected networks. A similar observation of another N1C2 sample at 10% sol dosage, shown in Figure 6f, further corroborates these findings. It is worth noting, that the individual elements are bulkier than the thin fibre-like structures of C-S-H observed in Figure 6a and Figure 6b, and should facilitate pore refinement and a stronger paste. The obtained findings strongly suggest the interaction of the sol-gel material with cement, and that it possibly acts as a seeding agent for the nucleation of C-S-H. Indeed, the energy plot of the calorimetry data (Figure 5) showed the highest amount of total energy evolved at the early stage for the 10% dose, indicative of additional nucleation, but subsequent retardation was noted. Perhaps, the paste 'recovered' during the curing process. However, optimising the sol to mitigate the retardation effect could lead to better control over the formation of such a microstructure or perhaps lead to even more unique morphologies.



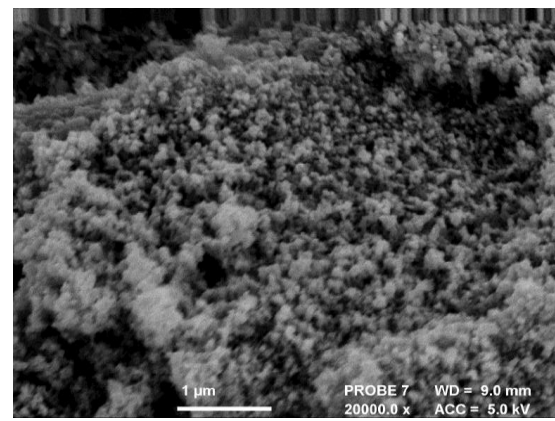
a) Control C2



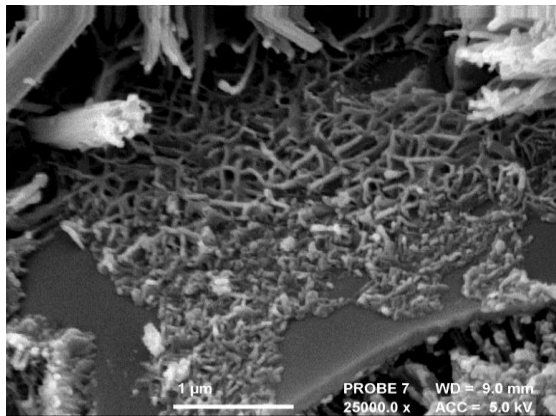
b) N1C2 Dose 1%



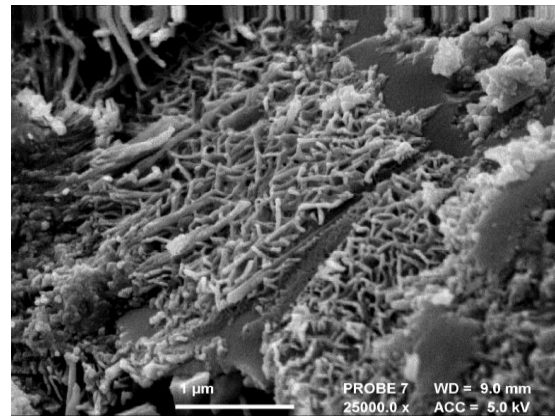
c) N1C2 Dose 5%



d) N1C2 Dose 5%



e) N1C2 Dose 10%



f) N1C2 Dose 10%

Figure 6 -SEM micrographs at 28 days showing differences in ~~morphology~~ morphology at high magnification.

CONCLUSIONS

The effect of sol-gel material on cement hydration was investigated. Initial findings based on calorimetric data suggested that alcohol ~~(as a sol-gel solvent or sol-gel by-product)~~ primarily ‘inhibits’ cement hydration whereas an acidic sol ‘delays’ the hydration processes. For cement pastes with the optimised and ~~alcohol~~ solvent-free synthesised sols, the data further supports that pH alone is not the limiting parameter. The optimised acidic and basic sols, both, exhibited similar trends concerning early hydration kinetics. The solvent-free synthesised sol appeared to accelerate cement hydration and indicated enhanced nucleation of C-S-H. SEM micrographs showed distinct morphologies of C-S-H, changing from isolated ‘thin’ fibre-like, ~~to structures to a dense granular form and lastly of C-S-H to reticular C-S-H more complex structures. The latter being a results in which the C-S-H is reticular (development~~ of a more intricate network of the silicates), particularly at higher sol dosages. The development of a complex network of C-S-H with bulkier elements than the control was observed on a portlandite crystal. The findings so far suggest that the silicate species introduced by the sol-gel material provided additional nucleation sites for C-S-H precipitation.

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